

IN SITU PLANETARY MINERALOGY USING SIMULTANEOUS TIME RESOLVED FLUORESCENCE AND RAMAN SPECTROSCOPY. J. Blacksborg¹ and G.R. Rossman², ¹Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena, CA 91109, Jordana.blacksberg@jpl.nasa.gov, ²California Institute of Technology, Division of Geological and Planetary Sciences, Pasadena, California 91125, grr@gps.caltech.edu

Introduction: Micro-Raman spectroscopy is one of the primary methods of mineralogical analysis in the laboratory, and more recently in the field. Because of its versatility and ability to interrogate rocks in their natural form (Figure 1), it is one of the frontrunners for the next generation of *in situ* instruments designed to explore a diverse set of solar system bodies (e.g. Mars, Venus, the Moon, and other primitive bodies such as asteroids and the Martian moons Phobos and Deimos), as well as for pre-selection of rock and soil samples for cache and return missions.

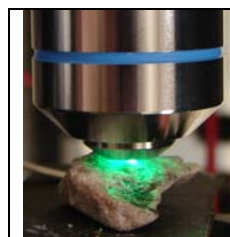


Figure 1. Image of our pulsed 532nm laser focused on a natural mineral sample without prior sample preparation. The Raman and fluorescence spectra are collected and sent to the spectrometer through the same objective lens.

Fluorescence spectroscopy offers complementary information revealing the many impurity and defect states present in minerals [1]. For a typical continuous wave (CW) green Raman measurement, fluorescence is viewed as a nuisance and is often so strong that the weaker Raman signal cannot be distinguished above the background. We discuss the use of time resolution to obtain Raman spectra under even the most extreme fluorescence conditions [2]. Since Raman occurs instantaneously, and fluorescence decay times vary, it is possible to separate them using time resolution (Figure 2). In addition to obtaining fluorescence-free Raman, we can distinguish the fluorescence spectra as well as any other time-dependent phenomena that may be present such as laser induced breakdown spectroscopy (LIBS) when performed under appropriate conditions.

Time Resolved Spectroscopy for Planetary mineralogy: Raman spectroscopy is under consideration for a host of landed planetary missions aimed at definitive mineralogical studies. For example on Mars, evidence for an early water rich history is supported by the probable presence of altered minerals such as goethite, jarosite, Fe-, Mg-, and Ca- sulfates, hydrated sulfates (e.g., kieserite), phyllosilicates (e.g., clays), and Fe-, Mg-, and Ca- carbonates [3]. Because many of these altered minerals are known to exhibit strong fluorescence, the use of time resolution would be expected to significantly improve the number of successful measurements on Mars. We demonstrate this

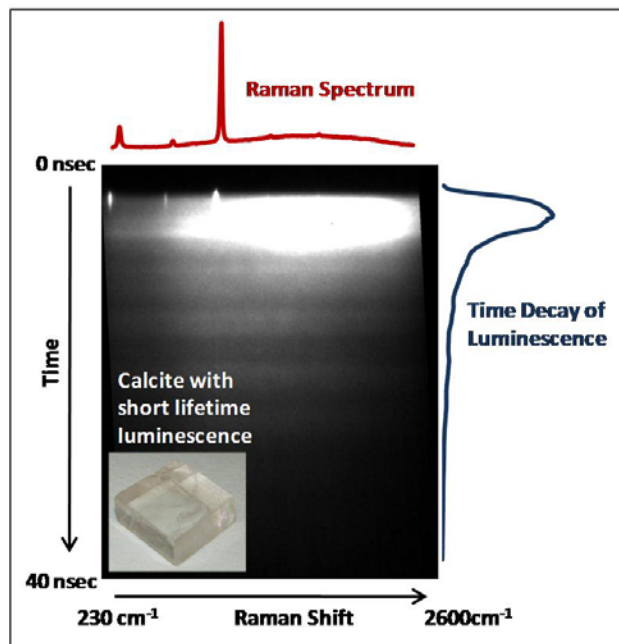


Figure 2. Streak Camera Image taken on a natural calcite sample with short lifetime fluorescence. The Raman spectrum is distinguishable during the laser pulse, and the fluorescence lifetime is ~ 8 ns.

technique using a green pulsed miniature microchip laser synchronized with a streak camera. We will discuss spectra obtained on a variety of strongly fluorescent altered minerals, with particular relevance to Mars (e.g. sulfates, phosphates, and clays). For many of these minerals Raman spectra were completely obscured by large background fluorescence when using CW Raman. We will conclude with a discussion of the challenges and feasibility of developing an on-surface time resolved spectrometer for planetary exploration.

Acknowledgements: The research described in this publication was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration. CW Raman measurements were performed at the California Institute of Technology, and time-resolved experiments at JPL.

References: [1] M. Gaft et al., *Modern Luminescence Spectroscopy of Minerals and Materials*, Springer-Verlag, 2005. [2] J. Blacksborg, G. Rossman, and A. Gleckler (2010) *Applied Optics*, 49 (26), 4951-4962, [3] D.W. Ming et al. (2008) in *The Martian Surface: Composition, Mineralogy and Physical Properties*, J.F. Bell III, ed., 519-540